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- (71) **Applicants
SKW Trostberg AG,
(FR Germany),
Postfach 1150-1160,
D-8223 Trostberg,
Federal Republic of
Germany.**
- (72) **Inventors
Werner Gmohling,
Georg Christian
Kreutzberger.**
- (74) **Agent and/or Address for Service
Abel and Imray,
Northumberland House,
303-306 High Holborn,
London WC1V 7LH.**
- (54) (Process for purifying silicon)**
- (57) A process for purifying silicon; to use in solar cells; by treating crude, or metallurgical grade, silicon with a molten slag comprising an alkaline earth metal, oxide(s) and/or alkali metal oxide(s) wherein the crude silicon is mixed in comminuted form with the slag or the slag components before melting is carried out.**

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SPECIFICATION

Process for purifying silicon

- 5 The invention relates to a process for purifying silicon, especially for the purpose of manufacturing solar-quantity silicon. 5

As a result of the increasing importance of solar cells in the production of energy, there have recently been various attempts to purify industrial silicon having a purity of at least 95 %, so-called crude silicon, in such a manner that it is suitable for manufacturing solar cells.

- 10 CH-PS 567 435 and US-PS 2 972 521 describe the purification of crude silicon using acids or mixtures of acids. However, it is not possible to remove certain impurities, such as, for example, boron or phosphorus, using these. 10

- DE-PS 1 022 806 and DE-OS 2 706 175 describe processes in which purification is carried out with the aid of a slag treatment such as, for example, with the aid of a silicate melt; in these processes, however, the purifying effect is restricted to the elements calcium and aluminium. 15

Even with a combination of the acid and slag treatments described, it is not possible to obtain silicon in a form suitable for manufacturing solar cells. For example, according to DE-OS 2 729 464, the crude silicon is brought into contact with an extraction melt before the acid treatment; nevertheless it is not possible in this way to remove, for example, the elements boron or phosphorus.

- 20 Although processes whose purifying action extends to all undesired foreign bodies have also been described, they are either too complex, and thus too uneconomical, or do not produce the desired degree of purity. In DE-OS 2 933 164, for example, a multi-stage process is described in which the extraction melting process is followed by an acid treatment and a vacuum treatment, but, even after melting and solidifying for a second time, only a moderate, and in no way adequate, purifying effect can be achieved in respect of boron. 25

The process described in DE-OS 2 944 975, in which silicon is reacted in the molten state with barium carbonate, provides a sufficient degree of purity in respect of boron, but, because of the very high temperatures required and the need additionally to blow in an oxidising gas, e.g. oxygen, or steam, in order to obtain a sufficient degree of purity, it is very labour- and cost-intensive.

- 30 There is therefore a need for a process for purifying silicon which does not possess the disadvantages indicated and by means of which silicon can be obtained, in a simple, economical manner not requiring a great amount of work, which possesses the purity required for manufacturing solar cells, especially purity in respect of boron. 30

- The present invention provides a process for the purification of crude silicon by treatment with a molten slag comprising an alkali metal oxide or alkaline earth metal oxide or a mixture of two or more thereof, which comprises mixing crude silicon in comminuted form with at least a part of the slag and/or component(s) which when molten would form the slag, before melting is carried out. 35

The term "crude silicon" is to be understood to include, for example, metallurgical crude silicon, which may have, for example the following composition:

40	95	-	99	%	Si	40
	0.2	-	1	%	Fe	
45	0.2	-	1.5	%	Al	45
	0.3	-	0.4	%	Ca	
	0.05	-	0.3	%	Ti	

- 50 or < 0.02 % Ti by selecting a particular grade of quartz. Usually the silicon content is 97 to 99 %. See also Ullmanns Encyklopädie der technischen Chemie, 4, Band 21, page 426 and Durrer/Volkert, Metallurgie der Ferrolegerungen, G. Volkert, K. -D. Frank, Springer-Verlag, 2, pages 529, 532 and 533. 50

- The slag denotes an oxide or oxide mixture or composition comprising oxide(s); the substances must be substantially pure and, especially, substantially free from boron and phosphorus. 55

- By treatment with a melt comprising the above oxide(s) it is possible to achieve a purification of the silicon such that it is suitable for manufacturing solar cells.

- Instead of the oxides it is also possible to use as slag-forming agents compounds which can be converted into the oxides under the conditions used, such as, for example, the carbonates and hydroxides of alkali metals and alkaline earth metals, which are converted to the oxides by splitting off carbon dioxide or water. Other compounds may also be suitable, e.g. the corresponding oxalates. 60

- It is also possible to use mixtures of two or more alkali metal and/or alkaline earth metal compounds.

- The alkaline earth metal compounds used are especially magnesium oxide, calcium oxide, strontium oxide and/or barium oxide, and/or the carbonates and/or hydroxides producing these oxides, and the alkali metal compounds are especially lithium oxide, sodium oxide and/or potassium oxide, and/or the 65

corresponding carbonates and/or hydroxides.

The process may advantageously be carried out in the presence of a suitable flux, such as, for example, magnesium fluoride and/or calcium fluoride, and/or in the presence of a diluent, such as, for example, oxides of metals in the 2nd to 4th groups of the Periodic Table. A suitable diluent for alkaline earth metal oxides is, for example, an oxide of a group IV metal, e.g. silica; and a suitable diluent for alkali metal oxides is, for example, an oxide of a group II to IV metal, e.g. alumina or/and silica.

The slag preferably comprises

(i) from 20 to 100 %, especially 20 to 65 %, by weight of alkali metal oxide and/or alkaline earth metal oxide or slag-forming component(s),

(ii) from 0 to 40 %, especially 0 to 20 %, by weight of flux and

(iii) from 0 to 80 % by weight of diluent.

The slag advantageously comprises selected raw material(s) such that the boron content in the slag is no more than, preferably less than, 10 ppm and, if necessary, the phosphorus content no more than, preferably less than, 100 ppm. Thus, for example, the slag may be a pure oxide or mixture thereof or substance(s) which can be converted into oxide(s) under the conditions used.

Accordingly, the present invention also provides a process for the purification of crude silicon by treatment with a molten slag comprising an oxide or oxide mixture wherein the content of boron is no greater than 10 ppm and preferably the content of phosphorus is no greater than 100 ppm, which comprises mixing the crude silicon in comminuted form with at least a part of the slag and/or component(s) which when molten would form the slag, before melting is carried out.

The average particle size of the comminuted crude silicon is preferably from 10 μm to 1 mm, especially from 40 μm to 100 μm . The comminution of the crude silicon metal may be effected, for example, by grinding in suitable mills, such as, for example, in centrifugal ball mills or counter-jet mills (particle size from approximately 10 to 100 μm), or by crushing (particle size ≤ 1 mm).

The slag or part thereof may, for example, also be comminuted before use. Generally, the grain size of the slag should be comparable with that of the comminuted silicon.

The average particle size of the slag or slag-forming component(s) is preferably also from 10 μm to 1 mm, especially from 40 μm to 100 μm . Thus, the slag or slag-forming component(s) may have the same grain spectrum as the comminuted crude silicon. Thus, for example, the slag or slag-forming component(s) may be comminuted as described above for the silicon. It is therefore also possible to carry out the comminution of the crude silicon and the slag or slag-forming component(s) together. This greatly assists in ensuring intensive mixing of the silicon and slag or slag-forming components.

If the components of the slag which are mixed together have a fine grain size no further comminuting, milling etc. is necessary.

The process may be carried out, for example, by mixing the comminuted crude silicon intensively with the total amount of the likewise comminuted slag and/or slag-forming component(s) and then melting this mixture, or by mixing the crude silicon with only part, for example a third to two thirds, of the comminuted slag or slag-forming component(s) and adding this mixture to the other, molten, part of the slag. In a preferred embodiment, the comminuted crude silicon is mixed with approximately half the slag or slag-forming component(s) and this mixture is then added, preferably slowly, to the other, molten, half. The two parts of the slag may have the same or different composition. Usually, however, the alkali metal oxide or alkaline earth metal oxide or slag-forming component(s) are present in both parts.

Melting may be effected in a customary furnace suitable for the purpose, such as, for example, in an electrical resistance furnace or an induction furnace. The melting temperature is usually from 1400 to 1600°C, especially approximately 1500°C.

The ratio of crude silicon to slag or slag-forming component(s) may be, for example, 1 : 0.2 to 1 : 4, especially 1 : 0.3 to 1 : 3. Thus, preferably, the ratio of silicon to alkaline earth metal oxide and/or alkali metal oxide is 1 : 0.2 to 4, especially 1 : 0.3 to 3.

After all the solid constituents are completely molten, the silicon melt may be drained or poured off. A longer residence time is generally unnecessary. However, in order to obtain silicon having an especially high degree of purity, it may be advantageous for the process according to the invention to be followed by a known acid treatment and/or vacuum treatment as described, for example, in DE-OS 29 33 164.

By means of the process according to the invention it is possible, surprisingly, to obtain silicon which has a much higher degree of purity than silicon obtained by previous slag treatment methods. It is possible, especially, to reduce the boron content of the crude silicon from approximately 40 ppm to approximately 3 to 4 ppm. It is thus possible by means of the process of the invention to obtain in a simple and economical manner silicon which, because of its purity, is very suitable for manufacturing solar cells.

The following Examples illustrate the invention.

60 Example 1

2.0 kg of metallurgical grade silicon of the customary composition were ground to a mean particle size of 40 μm , mixed intensively with 5.5 kg of a slag having a grain size of 10 to 600 μm consisting of 41 % by weight of magnesium oxide, 41 % by weight of silica and 18 % by weight of calcium fluoride and having a boron content of ≤ 10 ppm and added slowly to a further 5.5 kg of an already molten slag. After subsequent acid purification, the silicon had the following purity:

Iron 0.003 % by weight

Aluminium 0.0015 % by weight

Calcium ≤ 0.01 % by weight

Boron 3 ppm.

Example 2

1.0 kg of metallurgical grade silicon of the customary composition was crushed to a mean particle size of ≤ 1 mm, mixed intensively with 2.75 kg of a slag having a grain size of 10 to 600 μm consisting of 41 % by weight of barium hydroxide, 41 % by weight of silica and 18 % by weight of calcium fluoride and having a boron content of ≤ 10 ppm and added slowly to a further 2.75 kg of an already molten slag. After subsequent acid purification, the silicon had the following purity:

Aluminium < 0.01 % by weight

Calcium < 0.01 % by weight

Boron 2 ppm.

Example 3

1.0 kg of metallurgical grade silicon of the customary composition was ground to a mean particle size of 40 μm , mixed intensively with 2.8 kg of a slag having a boron content of ≤ 10 ppm consisting of 50 % by weight of sodium hydroxide of grain size ≤ 1 mm and 50 % by weight of silica of an average grain size of 100 μm and added slowly to a further 2.8 kg of an already molten slag. After subsequent acid purification, the silicon had the following purity:

Iron < 0.02 % by weight

Aluminium < 0.01 % by weight

Calcium < 0.01 % by weight

Boron 1 ppm.

Comparison example

When the metallurgical grade silicon used in Examples 1 to 3 was subjected to a slag treatment in the manner known hitherto, by adding the crude silicon to the already molten slags of Examples 1 to 3, the silicon obtained had the following purity after subsequent acid treatment:

Iron 0.01 % by weight

Aluminium 0.02 % by weight

Calcium 0.01 % by weight

Boron 36 ppm.

50 CLAIMS

1. A process for the purification of crude silicon by treatment with a molten slag comprising an alkali metal oxide or alkaline earth metal oxide or two or more such oxides, which comprise mixing the crude silicon in comminuted form with the slag and/or a component(s) which when molten would form the slag, before melting is carried out.
2. A process as claimed in claim 1, wherein the boron content of the slag is no more than 10 ppm.
3. A process as claimed in claim 1 or claim 2, wherein the phosphorus content of the slag is no more than 100 ppm.
4. A process as claimed in any one of claims 1 to 3, wherein the comminuted crude silicon is mixed with the total amount of comminuted slag or slag-forming component(s) and melted.
5. A process as claimed in any one of claims 1 to 3, wherein the comminuted crude silicon is mixed with part of the comminuted slag or slag-forming component(s) and this mixture is added to the remainder of the slag, which is molten.
6. A process as claimed in claim 5, wherein the comminuted crude silicon is mixed with approximately half of the slag or slag-forming component(s) and added to the other half of the slag, which is molten.

7. A process as claimed in any one of claims 1 to 6, wherein the slag comprises an oxide, carbonate or hydroxide of an alkali metal or alkaline earth metal or mixture of two or more such compounds.
8. A process as claimed in any one of claims 1 to 7, carried out in the presence of a flux.
9. A process as claimed in claim 8, wherein the flux is magnesium fluoride or calcium fluoride.
- 5 10. A process as claimed in any one of claims 1 to 9, carried out in the presence of an oxide diluent. 5
11. A process as claimed in claim 10, wherein the slag comprises an alkaline earth metal oxide and silica diluent, or an alkali metal oxide and aluminium oxide and/or silica diluent.
12. A process as claimed in any one of claims 1 to 11, wherein the slag comprises from 20 to 100 % by weight of alkali metal oxide(s) and/or alkaline earth metal oxide or an amount of component which when molten would form this amount of oxide, from 0 to 40 % by weight of flux and from 0 to 80 % by weight of diluent. 10
13. A process as claimed in any one of claims 1 to 12, wherein the alkaline earth metal oxide(s) are magnesium oxide, calcium oxide, strontium oxide and/or barium oxide.
14. A process as claimed in any one of claims 1 to 13, wherein the alkali metal oxide(s) are lithium oxide, sodium oxide and/or potassium oxide. 15
15. A process as claimed in any one of claims 1 to 14, wherein the average particle size of the comminuted crude silicon is from 10 μm to 1 mm.
16. A process as claimed in claim 15, wherein the average particle size of the comminuted crude silicon is from 40 μm to 100 μm .
- 20 17. A process as claimed in any one of claims 1 to 16, wherein the average particle size of the slag or slag-forming component(s) is from 10 μm to 1 mm. 20
18. A process as claimed in claim 17, wherein the average particle size of the slag or slag-forming component(s) is from 40 μm to 100 μm .
19. A process as claimed in any one of claims 1 to 18, wherein melting is carried out at a temperature of from 1400 to 1600°C. 25
20. A process as claimed in any one of claims 1 to 19, wherein the weight ratio of crude silicon to alkaline earth metal oxide and/or alkali metal oxide is from 1 : 0.2 to 1 : 4. 25
21. A process as claimed in claim 20, wherein the weight ratio of crude silicon to alkaline earth metal oxide and/or alkali metal oxide is from 1 : 0.3 to 1 : 3.
- 30 22. A process as claimed in any one of claims 1 to 21, wherein the crude silicon is metallurgical grade silicon. 30
23. A process as claimed in any one of claims 1 to 22, which includes a purifying vacuum treatment or acid treatment of the silicon.
24. A process as claimed in claim 1, carried out substantially as described in any one of Examples 1 to 3 herein. 35
25. Silicon, whenever purified by a process as claimed in any one of claims 1 to 24. 35